MOLECULAR-SCALE INTERROGATION OF CATALYTIC INTERACTIONS BETWEEN OXYGEN AND COBALT PHTHALOCYANINE USING ULTRAHIGH VACUUM TIP-ENHANCED RAMAN SPECTROSCOPY

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Ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) is a powerful method combining the rich chemical information of vibrational spectroscopy with the ultrahigh spatial resolution of scanning tunneling microscopy (STM). However, despite of its potential, there is a lack of studies demonstrating the capability of UHV-TERS in investigating chemical reactions and molecular adsorptions under controlled environment. Herein, we use UHV-TERS to investigate adsorption of oxygen (O_2) with cobalt (II) phthalocyanine (CoPc) supported on Ag(111) single crystal surfaces under highly controlled environment, which is the initial step for the oxygen reduction reaction (ORR) using metal Pc catalysts. Two adsorption configurations are primarily observed, assigned as O_2/CoPc/Ag(111) and O/CoPc/Ag(111) based on STM imaging, TERS, isotopologue substitution, and density functional theory (DFT) calculations. Distinct vibrational features are observed for different adsorption configurations such as the ^{18}O-^{18}O stretching frequency at 1151 $\mathrm{cm}^{-1}$for O_2/CoPc/Ag(111), and Co-^{16}O and Co-^{18}O vibrational frequencies at 661 $\mathrm{cm}^{-1}$and 623 cm^{-1}, respectively, for O/CoPc/Ag(111). DFT calculations show vibrational mode coupling of O-O and Co-O vibrations to the Pc ring, resulting in different symmetries of oxygen-related normal modes for different isotopes. This study establishes UHV-TERS as a chemically sensitive tool for probing catalytic systems at the molecular-scale.